ANODIC ACTIVE MATERIAL FOR A LITHIUM ION SECONDARY BATTERY
[Richiumu Ion Niji Denchi Yō Seikyoku Katsu Busshitsu]

Yukio Matsubara, Masami Ueda, and Kazuhiko Kikuya

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INVENTOR(S)	(72):	Yukio Matsubara, Masami Ueda, and Kazuhiko Kikuya
APPLICANT(S)	(71):	Fuji Chemical Industry Co., Ltd.
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Patent Claims

Claim 1

An anodic active material for a lithium ion secondary battery comprising of a lithium-nickel composite oxide expressed by the following general formula (1):

$$Li_y(Ni_{1-(a+b+c)}Co_aAl_bMn_c)_{1-d}B_dO_2 \quad ... \quad (1)$$

(In the figure, y, a, b, c, and d express the respective compositional ratios of Li, Ni, Co, Al, Mn, and B, whereas y satisfies $0.9 \leq y \leq 1.3$, whereas a, b, and c collectively satisfy $0.1 < (a + b + c) \leq 0.3$, whereas a satisfies $0.01 < a \leq 0.2$, whereas b satisfies $0.01 < b \leq 0.1$, whereas c satisfies $0.01 < c \leq 0.1$, whereas d satisfies $0 \leq d \leq 0.03$).

Claim 2

A method for manufacturing an anodic active material for a lithium ion secondary battery comprising of a lithium-nickel composite oxide expressed by the following general formula (1):

$$Li_y(Ni_{1-(a+b+c)}Co_aAl_bMn_c)_{1-d}B_dO_2 \quad ... \quad (1)$$

(In the figure, y, a, b, c, and d express the respective compositional ratios of Li, Ni, Co, Al, Mn, and B, whereas y satisfies $0.9 \leq y \leq 1.3$, whereas a, b, and c collectively satisfy $0.1 < (a + b + c) \leq 0.3$, whereas a satisfies $0.01 < a \leq 0.2$, whereas b satisfies $0.01 < b \leq 0.1$, whereas c satisfies $0.01 < c \leq 0.1$, whereas d satisfies $0 \leq d \leq 0.03$) characterized, in a case where no boron is included ($d = 0$), not only by the addition, to a basic metal salt expressed by the following general formula (2):
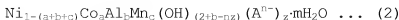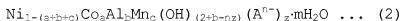
$$Ni_{1-(a+b+c)}Co_aAl_bMn_c(OH)_{(2+b-nz)}(A^{n-})_z \cdot mH_2O \quad ... \quad (2)$$

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(In the formula, A^{n-} signifies an n-valent (n = 1 ~ 3) anion, whereas z and m are each positive numbers respectively satisfying ranges of $0.03 \leq z \leq 0.3$ and $0 \leq m < 2$) within an aqueous medium, of a lithium compound at a quantitative ratio equivalent to the lithium atom molar number expressed by y but also by the fact that the obtained slurry is spray- or freeze-dried and then baked within an oxidative atmosphere at approximately 600 ~ 900°C for at least approximately 4 hours.

<u>Claim 3</u>

A method for manufacturing an anodic active material for a lithium ion secondary battery comprising of a lithium-nickel composite oxide expressed by the following general formula (1):

$$Li_y(Ni_{1-(a+b+c)}Co_aAl_bMn_c)_{1-d}B_dO_2 \ ... \ (1)$$

(In the figure, y, a, b, c, and d express the respective compositional ratios of Li, Ni, Co, Al, Mn, and B, whereas y satisfies $0.9 \leq y \leq 1.3$, whereas a, b, and c collectively satisfy $0.1 < (a + b + c) \leq 0.3$, whereas a satisfies $0.01 < a \leq 0.2$, whereas b satisfies $0.01 < b \leq 0.1$, whereas c satisfies $0.01 < c \leq 0.1$, whereas d satisfies $0 \leq d \leq 0.03$) characterized, in a case where boron is included (d ≠ 0), not only by the additions, to a basic metal salt expressed by the following general formula (2):

$$Ni_{1-(a+b+c)}Co_aAl_bMn_c(OH)_{(2+b-nz)}(A^{n-})_z \cdot mH_2O \ ... \ (2)$$

(In the formula, A^{n-} signifies an n-valent (n = 1 ~ 3) anion, whereas z and m are each positive numbers respectively satisfying ranges of $0.03 \leq z \leq 0.3$ and $0 \leq m < 2$) within an aqueous medium, of a boron compound at a quantitative ratio equivalent to the boron atom molar number expressed by d, and then of a lithium

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compound at a quantitative ratio equivalent to the lithium atom molar number expressed by y but also by the fact that the obtained slurry is spray- or freeze-dried and then baked within an oxidative atmosphere at approximately 600 ~ 900°C for at least approximately 4 hours.

Claim 4

A manufacturing method characterized by the fact that the spray- or freeze-dried product obtained in Claim 2 or 3 is press-molded and then baked within an oxidative atmosphere at approximately 600 ~ 900°C for at least approximately 4 hours.

Claim 5

A non-aqueous electrolytic solution lithium ion secondary battery, which is a non-aqueous electrolytic solution lithium ion secondary battery comprising of an anode inclusive of an anodic active material, a cathode capable of doping and dedoping lithium, and a non-aqueous electrolyte provided by solubilizing a lithium salt into a non-aqueous medium and is characterized by the fact that the aforementioned anodic active material is a lithium-nickel composite oxide expressed by the following general formula (1):

$$Li_y(Ni_{1-(a+b+c)}Co_aAl_bMn_c)_{1-d}B_dO_2 \ ... \ (1)$$

(In the figure, y, a, b, c, and d express the respective compositional ratios of Li, Ni, Co, Al, Mn, and B, whereas y satisfies $0.9 \leq y \leq 1.3$, whereas a, b, and c collectively satisfy $0.1 < (a + b + c) \leq 0.3$, whereas a satisfies $0.01 < a \leq 0.2$, whereas b satisfies $0.01 < b \leq 0.1$, whereas c satisfies $0.01 < c \leq 0.1$, whereas d satisfies $0 \leq d \leq 0.03$).

<u>Detailed explanation of the invention</u>

[0001]

(Technical fields to which the invention belongs)

The present invention concerns an anodic active material for a lithium ion secondary battery with improved recharge and discharge efficiencies and a potential, at the time of a discharge, as well as a non-aqueous electrolytic solution lithium ion secondary battery inclusive of an anode comprising of said anodic active material.

[0002]

(Prior art)

In recent years, demands for light-weight lithium ion secondary batteries, bearing high energy densities and predicted to replace nickel-cadmium batteries and nickel-hydrogen batteries, have been intensifying in accordance with the entrenchment of compact and portable electronic appliances. As anodic active materials of such lithium ion secondary batteries, $LiNiO_2$ and $LiCoO_2$, which are laminar compounds capable of intercalating and deintercalating lithium ions, have been known. Of these, the expectation for $LiNiO_2$ is high, since it bears an electric capacitance higher than that of $LiCoO_2$ and is low in cost. Despite the high capacitance of the $LiNiO_2$, however, its discharge and recharge cycle characteristics, high-temperature stability, etc. are problematic, and therefore, various improvements have been investigated. The crystalline structure of $LiNiO_2$, in particular,

becomes unstable as a result of the dissociation, from a crystal, of profuse lithium ions at the time of a recharge, and since the laminar structure becomes disturbed as a result of the rearrangement of ions, undesirable effects become exerted onto the cycle characteristics. Methods for partially substituting nickel with other elements have been known in the context of ameliorating such crystalline structure disturbances, whereas a research embodiment attempting to improve cycle characteristics by partially substituting nickel with another element(s) (e.g., cobalt, etc.) is reported by *Electrochimica Acta*, 38 (9), 1159 (1993). Moreover, the stability of $LiNiO_2$ at the time of a recharge, above all, the high-temperature

stability thereof, is inferior to its counterpart of $LiCoO_2$. The reasons is because, in a case where a lithium ion secondary battery abiding in a recharge state becomes exposed to a high temperature (60°C or above), the battery anode becomes reacted with the electrolytic solution, whereas the reactivity of $LiNiO_2$ is said to be higher than that of $LiCoO_2$. As improved versions, *J. Electrochem. Soc.*, 144 (9), 3117 (1997) reports an embodiment for partially substituting nickel with cobalt, manganese, and/or titanium, whereas *J. Electrochem. Soc.*, 142 (12), 4033 (1995) reports an embodiment for partially substituting nickel with aluminum.

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[0003]

(Problems to be solved by the invention)

In the context of thus improving the cycle characteristics and high-temperature stabilities of $LiNiO_2$, the present inventors previously discovered and disclosed a partial substitution of nickel with at least one element selected from among cobalt, aluminum, manganese, iron, and boron (World Patent Kokai Gazette No. WO98/06670). This invention is peculiarly characterized, since many types of other substituting elements can, both simultaneously and easily, be solid-solubilized with nickel, by the addressing of various problems inherent in $LiNiO_2$. Although the aforementioned problems can be improved by solid-solubilizing many types of other substituting elements with nickel, however, the following problems arise. In a case where aluminum is added as an element for substituting nickel, in particular, the recharge-discharge efficiency (initial recharge capacitance/initial discharge capacitance) deteriorates. In a case where cobalt is added as a substituting element, furthermore, the potential at the time of a discharge decreases as the cobalt substituting ratio increases.

[0004]

The attenuation of the recharge-discharge efficiency is a grave problem from the standpoint of upping the capacitance of a lithium ion secondary battery in that the quantitative ratio of a cathode becomes upped on an occasion for preparing a battery, that the battery capacitance consequently becomes depleted in terms of unit volume comparison, and that the potential attenuation at the time of the discharge entails low per-energy results despite a

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high capacitance. These properties, too, must therefore be ameliorated in consideration of overall battery performances.

[0005]
(Mechanism for solving the problems)

The present inventors discovered, in the course of studies on anodic active materials, that the problems inherent in the $LiNiO_2$ of the prior art, namely cycle characteristics and high-temperature stability, can be ameliorated by optimizing combinations of nickel, cobalt, aluminum, and boron, although, conversely, such problems as the attenuation of a recharge-discharge efficiency and the attenuation of a potential at the time of a discharge have arisen. The present inventors compiled additional intensive researches and, as a result, discovered that it becomes possible, by adding, as a nickel substituting element, an optimal quantitative ratio of manganese together with cobalt, aluminum, and boron, to improve the recharge-discharge efficiency and to ameliorate a potential attenuation at the time of a discharge without compromising the cycle characteristics and high-temperature stability.

[0006]

In other words, the present invention provides an anodic active material for a lithium ion secondary battery comprising of a lithium-nickel composite oxide expressed by the following general formula (1):

$$Li_y(Ni_{1-(a+b+c)}Co_aAl_bMn_c)_{1-d}B_dO_2 \quad ... \quad (1)$$

(In the figure, y, a, b, c, and d express the respective compositional ratios of Li, Ni, Co, Al, Mn, and B, whereas y satisfies $0.9 \leq y \leq 1.3$, whereas a, b, and c collectively satisfy $0.1 < (a + b + c) \leq 0.3$, whereas a satisfies $0.01 < a \leq 0.2$, whereas b satisfies $0.01 < b \leq 0.1$, whereas c satisfies $0.01 < c \leq 0.1$, whereas d satisfies $0 \leq d \leq 0.03$).

[0007]

The lithium-nickel composite oxide of the present invention can be manufactured by solid-solubilizing, into nickel, substituting cobalt, aluminum, magnesium, and boron satisfying the relational formula (composition) expressed by the aforementioned general formula (1). Said lithium-nickel composite oxide is capable of improving the recharge-discharge efficiency and of inhibiting, at the time of a discharge, a potential loss without compromising favorable cycle characteristics and high-temperature stability and is therefore useful as an anodic active material attempting to up the energy of a lithium ion secondary battery.

[0008]

It is desirable for the internalization ratio of nickel, within the lithium-nickel composite oxide expressed by the aforementioned general formula (1), to be at least 0.68, for the battery capacitance thereof, as a nickel-type anodic active material becomes excessively low below this threshold.

[0009]

It is desirable for the cobalt substituting ratio and aluminum substituting ratio to be confined respectively to ranges of $0.01 < a \leq 0.2$ and $0.01 < b \leq 0.1$, whereas, as the cobalt

substituting ratio becomes higher and as the aluminum substituting ratio accordingly becomes lower, the cycle characteristics and recharge-discharge efficiency become improved, although it becomes impossible to guarantee the high-temperature stability, accompanied by a potential attenuation at the time of a discharge. Conversely, as the aluminum substituting ratio becomes higher and as the cobalt substituting ratio accordingly becomes lower, the high-temperature stability can be improved, although the cycle characteristics and recharge-discharge efficiency become problematic. It becomes possible, by providing a quaternary element substituting system by adding manganese to a ternary element substituting system of cobalt, aluminum, and boron, above all by partially substituting, with manganese, cobalt accounting for a high ratio of addition, not only to maintain a high-temperature stability proportional to the aluminum substituting ratio and conserve the utilization ratio of expensive cobalt but also to improve the cycle characteristics, recharge-discharge efficiency, and potential at the time of a discharge.

[0010]

There are no special restrictions on the substituting ratio range of the manganese of the present invention, for it differs depending on the respective utilization ratios of cobalt, aluminum, and boron for substituting nickel, although a range of $0.01 < c \leq 0.1$ is preferred, whereas a range of $0.025 \leq c \leq 0.06$ is more desirable from the standpoint of improving the recharge-discharge efficiency, whereas in a case where the ratio is lower than said range, no visible effects are acknowledged, whereas the

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efficiency somewhat drops in a case where the same is higher. It is desirable, from the standpoint of improving the potential in the course of recharge-discharge cycles, for the manganese substituting ratio to be confined to a range of $0.05 \leq c \leq 0.1$. In this case, no significant difference is acknowledged even if the substituting ratio is upped to 0.1, so long as it is at least 0.05.

[0011]

There are no special restrictions on the substituting ratio range of boron, for it differs depending on the respective utilization ratios of cobalt, aluminum, and manganese for substituting nickel, although a range of $0 \leq d \leq 0.03$ is preferred, for it becomes possible, within this range, to improve the battery performances (open circuit voltage attenuation and polarization attenuation) without compromising the cycle characteristics and high-temperature

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stability, in contrast with which the battery performances become inferior beyond the 0.03 threshold.

[0012]

It is therefore desirable for the respective nickel substituting ratios of cobalt, aluminum, manganese, and boron to be confined to the following ranges:

It is desirable for (1): a, b, and c to satisfy $0.1 < (a + b + c) \leq 0.3$, for (2): a to satisfy $0.01 < a \leq 0.2$, for (3): b to satisfy $0.01 < b \leq 0.1$, for (4): c to satisfy $0.01 < c \leq 0.1$, and for (5:) d to satisfy $0 \leq d \leq 0.03$.

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[0013]

(Application embodiments of the invention)

In the following, the anodic active material of the present invention for a lithium ion secondary battery will be concretely explained. The anodic active material of the present invention for a lithium ion secondary battery is a material capable, by partially substituting nickel with a solid-solubilized ternary element system of cobalt, aluminum, and boron bearing a specified compositional range, not only of improving the cycle characteristics and high-temperature stability but, by further partially substituting nickel with a solid-solubilized quaternary element system provided by partially substituting cobalt with manganese, also of ameliorating (inhibiting) the attenuation of the recharge-discharge efficiency and the attenuation, at the time of a discharge, of the potential, namely problems inherent in the aforementioned ternary element system. Reasons for these improvements have yet to be clarified, although the following speculations seem plausible. In a case where the nickel of $LiNiO_2$ becomes partially substituted with cobalt, the cycle characteristics and recharge-discharge efficiency become improved, although the potential, at the time of a discharge, decreases as the cobalt substituting ratio increases. In a case where the substituting share of the cobalt is partially substituted with manganese, therefore, it becomes possible to inhibit the potential at the time of the discharge in accordance with the lesser cobalt substituting ratio and to up the potential due presumably to the

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lower electroconductivity of manganese in comparison with nickel and cobalt. Moreover, in a case where, upon the partial substitution, with cobalt, of the nickel of the aforementioned $LiNiO_2$, the substituting share of cobalt is further substituted partially with aluminum, the high-temperature stability becomes improved, although the recharge-discharge efficiency deteriorates as the aluminum substituting ratio increases. In a case where, without altering the prevailing aluminum substituting ratio, the cobalt is further substituted partially with an optimal ratio of manganese, the recharge-discharge efficiency becomes improved due presumably to the stabilization of the $LiNiO_2$ structure. It accordingly becomes possible, by providing the quaternary element substituting system expressed by the general formula (1) of the present invention wherein the cobalt of a ternary element substituting system of nickel, cobalt, and aluminum, expressed by $Li_y(Ni_{1-(a+b)}Co_aAl_b)_{1-d}B_dO_2$, is partially substituted with manganese, to improve the recharge-discharge efficiency and potential at the time of discharge without compromising the cycle characteristics and high-temperature stability improved by the ternary element system. The optimal compositional ranges of the respective elements are confined to the range expressed by the general formula (1).

[0014]

The lithium-nickel composite oxide of the present invention can be obtained based on the following manufacturing method.

[0015]

The same can be concretely manufactured, (1): In a case where no boron is included (d = 0) within a lithium-nickel composite oxide expressed by the following general formula (1):

$$Li_y(Ni_{1-(a+b+c)}Co_aAl_bMn_c)_{1-d}B_dO_2 \; ... \; (1)$$

(In the figure, y, a, b, c, and d express the respective compositional ratios of Li, Ni, Co, Al, Mn, and B, whereas y satisfies $0.9 \leq y \leq 1.3$, whereas a, b, and c collectively satisfy $0.1 < (a + b + c) \leq 0.3$, whereas a satisfies $0.01 < a \leq 0.2$, whereas b satisfies $0.01 < b \leq 0.1$, whereas c satisfies $0.01 < c \leq 0.1$, whereas d satisfies $0 \leq d \leq 0.3$), by adding, to a basic metal salt expressed by the following general formula (2):
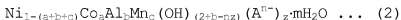
$$Ni_{1-(a+b+c)}Co_aAl_bMn_c(OH)_{(2+b-nz)}(A^{n-})_z \cdot mH_2O \; ... \; (2)$$

(in the formula, A^{n-} signifies an n-valent (n = 1 ~ 3) anion, whereas z and m are each positive numbers respectively satisfying ranges of $0.03 \leq z \leq 0.3$ and $3.0 \leq m < 2$) within an aqueous medium, a lithium compound at a quantitative ratio equivalent to the lithium atom molar number expressed by y and by spray- or freeze-drying and then baking the obtained slurry within an oxidative atmosphere at approximately 600 ~ 900°C for at least approximately 4 hours.

[0016]

The same can, furthermore, be manufactured, (2): In a case where boron is included (d ≠ 0), by adding, to a basic metal salt expressed by the following general formula (2):

$$Ni_{1-(a+b+c)}Co_aAl_bMn_c(OH)_{(2+b-nz)}(A^{n-})_z \cdot mH_2O \; ... \; (2)$$

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(In the formula, A^{n-} signifies an n-valent (n = 1 ~ 3) anion, whereas z and m are each positive numbers respectively satisfying ranges of $0.03 \leq z \leq 0.3$ and $3.0 \leq m < 2$) within an aqueous medium, a boron compound at a quantitative ratio equivalent a boron atom molar number expressed by d, by further adding, within an aqueous medium, lithium compound at a quantitative ratio equivalent to the lithium atom molar number expressed by y, and by spray- or freeze-drying and then baking the obtained slurry within an oxidative atmosphere at approximately 600 ~ 900℃ for at least approximately 4 hours. The spray dry method is then more desirable within the scope of the present invention. Ones inclusive of anions scheduled to become scattered at the time of baking can be favorably used as water-soluble lithium compounds and basic metal salts.

[0017]

One, two, or more types of lithium compounds may, for example, be selected from among LiOH, $LiNO_3$, Li_2CO_3, corresponding hydrates, etc.

[0018]

A_{n-} in the basic metal salt may, for example, be selected from among anions expressed by NO_3^-, Cl^-, Br^-, CH_3COO^-, CO_3^{2-}, SO_4^{2-}, etc.

[0019]

Of these compounds, LiOH and boric acid are desirable respectively as the lithium compound and boron compound from standpoints of yield, reactivity, effective resource utility, oxidation acceleration effects, etc., whereas the combination of

basic metal salts inclusive of nitric acid as an anion is especially desirable from the standpoint of battery performances.

[0020]

The basic metal salt used on this occasion can be manufactured by adding and reacting, to and with an aqueous solution of an $Ni_{1-(a+b+c)}Co_aAl_bMn_c$ salt, approximately 0.7 ~ 0.95 equivalent, preferably 0.8 ~ 0.95 equivalent, of an alkali under reaction conditions of approximately 80°C or below. Hereby usable alkali may, for example, be instantiated by hydroxides of alkali metals (e.g., sodium hydroxide,

etc.), hydroxides of alkaline earth metals (e.g., calcium hydroxide, etc.), amines, etc. Incidentally, it is more desirable for the basic metal salt thus synthesized to be ripened at 20 ~ 70°C for 0.1 ~ 10 hours. Subsequently, byproducts are removed by means of water washing, followed by the addition of a lithium compound and, in a case where a composite oxide inclusive of boron is manufactured, by the addition of a boron compound.

[0021]

Boric acid, lithium tetraborate, etc. can favorably be used as boron compounds.

[0022]

It is desirable for the slurry obtained as a result of the foregoing reaction to be dried based on the spray or freeze dry method.

[0023]

The spray dry method capable of yielding an instantaneously dried spherical product is desirable from standpoints of spherical granulation and compositional homogeneity (a heterogeneous composition becomes obtained based on a drying method requiring a prolonged drying time due to the migration of lithium to the surface thereof).

[0024]

The baking operation is executed within a temperature range of 600 ~ 900°C, preferably 750 ~ 850°C, within an oxygen stream for approximately 4 hours. It is more desirable for the duration to be confined to a range of 4 ~ 72 hours, preferably approximately 4 ~ 20 hours. In a case where the baking time is longer than 72 hours, not only does cost appreciation become unavoidable but, since the trivalent ratio of (Ni + Co + Mn) decreases in accordance with the evaporation of lithium, the product purity also becomes inferior.

[0025]

Considering that a baking period of at least 20 hours has been required for nickel, which cannot be easily converted into trivalent from divalent, based on a traditionally known technique related to this baking technique (e.g., dry method, etc.), the compound of the present invention can be obtained in an extremely economic fashion based on a simple manufacturing method.

[0026]

The press molding method is advantageous in a case where a high bulk density is targeted.

[0027]

It becomes possible, by press-molding a spray-dried product obtained by the aforementioned spray dry method into which microscopic quantitative ratios [of substituting elements?] have been homogeneously solubilized, for example, to obtain a composite oxide bearing a high bulk density as well as a high degree of crystallization and purity.

[0028]

A spherical spray-dried product is a powder excellent in terms of fluidity, moldability, and fillability and can be press-molded as it is based on an ordinary method.

[0029]

There are no special restrictions on the molding pressure, since it differs depending on press machines, feeding volumes, etc., although a range of approximately 500 ~ 3,000 kg/cm^2 is normally preferred. Pelletizers, briquette machines, roller compactors, etc. can favorably be used press molding machines, although there are no special restrictions on usable mechanisms, so long as they are capable of pressing.

[0030]

It is desirable for the density of the pressed product to be confined to a range of approximately 1 ~ 4 g/cc, preferably approximately 2 ~ 3 g/cc.

[0031]

The press molding is extremely useful from standpoints of abbreviating the inter-molecular mobilization distance and of accelerating the crystal growth at the time of baking. There is

therefore no need for the material subjected to press molding to
be a spherical spray-dried product, and a freeze-dried product can
likewise be used.

[0032]

The obtained press molded product is baked as it is. The
baking is normally executed within a temperature range of 600 ~
900°C, preferably 750 ~ 850°C, within an oxygen stream for at least
4 hours. The primary particle size becomes enlarged as the baking
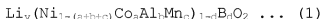time becomes longer, and therefore, the baking time is determined,
depending on desired primary particle sizes.

[0033]

The lithium-nickel composite oxide thus obtained expressed by
the aforementioned general formula (1) is capable of improving the
recharge-discharge efficiency and the potential at the time of a
discharge, without compromising the cycle characteristics and
high-temperature stability, namely problems disclosed by the
present inventors in World Patent Kokai Gazette No. WO98/06670,
and therefore, it can be used effectively as an anodic active
material for a lithium ion secondary battery.

[0034]

In other words, the non-aqueous electrolytic solution lithium
ion secondary battery of the present invention is a non-aqueous
electrolytic solution lithium ion secondary battery comprising of
an anode inclusive of an anodic active material, a cathode capable
of doping and dedoping lithium, and a non-aqueous electrolyte
provided by solubilizing a lithium salt into a non-aqueous medium
and is characterized by the fact that the aforementioned anodic

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active material is a lithium-nickel composite oxide expressed by the following general formula (1):

$$Li_y(Ni_{1-(a+b+c)}Co_aAl_bMn_c)_{1-d}B_dO_2 \quad \ldots \quad (1)$$

(In the figure, y, a, b, c, and d express the respective compositional ratios of Li, Ni, Co, Al, Mn, and B, whereas y satisfies $0.9 \leq y \leq 1.3$, whereas a, b, and c collectively satisfy $0.1 < (a + b + c) \leq 0.3$, whereas a satisfies $0.01 < a \leq 0.2$, whereas b satisfies $0.01 < b \leq 0.1$, whereas c satisfies $0.01 < c \leq 0.1$, whereas d satisfies $0 \leq d \leq 0.03$).

[0035]

As far as the method for preparing an anode by using said anodic active material is concerned, an anodic mixture composition is prepared by homogeneously mixing, for example, an anodic active material powder, an electroconductive material (e.g., carbon black, graphite, etc.), and a binder resin (e.g., polyvinylidene fluoride, etc.) based on an ordinary method, whereas a pellet-shaped anode for a coin-shaped secondary battery is prepared by compression-molding said composition.

[0036]

Moreover, it is also conceivable to prepare a pasty anodic active material by adding, together with the anodic active material powder and electroconductive material, a publicly known solvent (e.g., formamide, N-methylpyrrolidone, etc.) and to prepare an anode for a cylindrical or angular secondary battery by coating said mixture on an anodic collector and by then drying the same.

[0037]

The aforementioned anode can be used favorably for a non-aqueous electrolytic solution lithium ion secondary battery constituted by a cathode comprising of a material capable of doping and dedoping lithium (e.g., carbonaceous material, lithium alloy, etc.) and a non-aqueous electrolytic solution into which a lithium salt has become solubilized. Usable materials capable of doping and dedoping lithium may, for example, be instantiated by pyrolyzed carbons; cokes such as pitch coke, petroleum coke, needle coke, etc.; graphites; glassy carbons; baked organic polymer compounds obtained by baking phenol resins, furan resins, etc. at appropriate temperatures; carbonaceous materials such as carbon fibers, activated carbon, etc.; and/or polymers such as polyacetylene, polypyrrole, etc. Usable lithium alloys may, for example, be instantiated by a lithium-aluminum alloy.

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[0038]

In a case where a carbonaceous material is used as a cathode, for example, a cathodic mixture composition is prepared according to treatment procedures similar to those of a case where an anode is prepared (e.g., by homogeneously mixing a carbonaceous material powder and a binder resin comprising of polyvinylidene fluoride, etc.), and a pellet-shaped cathode for a coin-shaped secondary battery can be prepared by compression-molding the obtained composition. In a case where metallic lithium or a lithium alloy is used as a cathodic material, a cathode can be prepared by

mechanically punching a sheet-shaped metallic lithium or lithium alloy into a desired shape (e.g., pellet shape).

[0039]

It is conceivable to use, as the non-aqueous electrolytic solution constituting the non-aqueous electrolytic solution lithium ion secondary battery, either a non-aqueous electrolytic solution obtained by solubilizing and/or dispersing a lithium salt electrolyte into a publicly known non-aqueous medium (e.g., non-aqueous solvent, ion conductive polymer, etc.) or a solid electrolyte.

[0040]

Usable non-aqueous solvents for the non-aqueous electrolytic solution are instantiated by propylene carbonate, ethylene carbonate, butylene carbonate, vinylene carbonate, γ-butyrolactone, sulfolane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 2-methyltetrahydrofuran, 3-methyl-1,3-dioxolane, methyl propionate, methyl butyrate, dimethynole [sic: Presumably "dimethylene"?] carbonate, diethyl carbonate, dipropyl carbonate, etc. Only one type or combinations of two or more types of the aforementioned solvents may be used.

[0041]

Usable electrolytes may, for example, be instantiated by $LiClO_4$, $LiPF_6$, $LiAsF_6$, $LiBF_4$, $LiCF_3SO_3$, $LiN(CF_3SO_2)$, etc. Other constituent elements of the non-aqueous electrolytic solution lithium ion secondary battery (e.g., separator, battery can, etc.) are similar to their counterparts of non-aqueous electrolytic solution lithium ion secondary batteries of the prior art, and

there are no special restrictions. Likewise, there are no special restrictions on the shape of the battery, and arbitrary shapes, such as the cylindrical shape, angular shape, coin shape, button shape, etc., can be selected.

[0042]

In the following, the present invention will be explained in detail with reference to application examples.

(Application examples)

Application Example 1: A case where the nickel portion of $LiNiO_2$ is substituted with an Ni : Co : Al : Mn (molar ratio) = 80 : 10 : 5 : 5 composition

A mixed aqueous solution bearing a total (Ni + Co + Al + Mn) molar number of 4.0 M was prepared by using nickel nitrate, cobalt nitrate, aluminum nitrate, and manganese nitrate in such a way to realize an Ni : Co : Al : Mn (molar ratio) = 80 : 10 : 5 : 5 composition. Moreover, a 4.0 M sodium hydroxide solution was prepared, and a continuous reaction was induced at a reaction temperature of 25°C over a residing period of 15 min. by simultaneously charging, in an agitated state, both solutions into a reaction tank at an eventual pH of 9.5 by using a proportioning pump. The obtained reaction product was filtered, and after it had been washed with water (incidentally, a partially dried product bore a composition of $Ni_{0.8}Co_{0.1}Al_{0.05}Mn_{0.05}(OH)_{1.7}(NO_3)_{0.35} \cdot 0.22H_2O$) and then suspended into water, a slurry was obtained by adding, to the obtained suspension, boric acid at a quantitative ratio, with respect to the aforementioned Ni, Co, Al, and Mn, equivalent to

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(Ni + Co + Al + Mn) : B molar ratio = 99 : 1. After a 3.0 M aqueous lithium hydroxide solution had been added to this slurry, at a quantitative ratio equivalent to an Li/(Ni + Co + Al + Mn + B) = 1.05 molar ratio, the obtained mixture was spray-dried. The obtained dried gel was charged into an alumina board [sic: Presumably "boat"?] and then baked, while oxygen was being permeated within a tubular furnace (Model TF-630, manufactured by Yamada Electric Co.), within a temperature range of 750 ~ 850°C over a 15-hour period. An X-ray diffraction analysis of the baked product yielded a pattern analogous to its counterpart registered in 09-0063 ($LiNiO_2$) of the Joint Committee on Powder Diffraction Standards (hereafter abbreviated as "JCPDS"), whereas no peaks other than a peak attributed to $LiNiO_2$ were acknowledged, based on which the pervasion of a crystalline structure, similar to its counterpart of $LiNiO_2$, provided by homogeneously solid-solubilizing, into nickel, components other than nickel, was verified (Figure 2).

[0043]

Preparation of an anode: At the initial step of anode preparation, the anodic active material, acetylene black, which served as an electroconductivizing agent, and Teflon, which served as a binder, were mutually mixed at a weight ratio of 70 : 20 : 10, and after 75 mg of the obtained anodic agent had been compression-molded into a pellet with a diameter of 18 mm at 3 ton/cm^2, punched into a diameter of 16 mm, and then sufficiently dried, an anode was obtained. A cross-sectional view of a battery

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manufactured by using the electrode thus prepared is shown in Figure 1.

[0044]

The aforementioned anode (7) was used for assembling a Model 2032 coin battery within a globe box of an argon atmosphere. A metallic lithium sheet with a diameter of 15 mm and a thickness of 1 mm was used as a cathode (2), whereas a 1 : 2 mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) inclusive, as a support electrolyte, of 1 mole of $LiPF_6$ was used as an electrolytic solution.

[0045]

The battery thus prepared was subjected to a recharge-discharge test within a battery [sic: Presumably "voltage"?] range of 3.0 V ~ 4.3 V at a current density of 0.4 mA/cm^2. The respective results on the initial recharge-discharge efficiency and initial recharge-discharge curve are shown in Table I and Figure 5.

[0046]

Application Example 2: A case where the nickel portion of $LiNiO_2$ is substituted, without including boron, with a composition otherwise identical to its counterpart of Application Example 1

After a 3.0 M aqueous lithium hydroxide solution had been added to the reaction slurry obtained in Application Example 1 at a quantitative ratio equivalent to an Li/(Ni + Co + Al + Mn) = 1.05 molar ratio, the obtained mixture was spray-dried. The obtained dried gel was charged into an alumina board [sic:

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Presumably "boat"?] and then baked, while oxygen was being permeated within the aforementioned tubular furnace, within a temperature range of 750 ~ 850°C over a 15-hour period. An X-ray diffraction analysis of the baked product yielded a pattern analogous to its counterpart registered in 09-0063 of the JCPDS, whereas no peaks other than the peak attributed to $LiNiO_2$ were acknowledged, based on which the pervasion of a crystalline structure similar to its counterpart of $LiNiO_2$ provided by homogeneously solid-solubilizing, into nickel, components other than nickel was verified (Figure 2). Moreover, a battery was prepared based on a method similar to its counterpart of Application Example 1, and a recharge-discharge test was conducted under identical conditions. The respective results on the initial recharge-discharge efficiency and initial recharge-discharge curve are shown in Table I and Figure 6.

[0047]

Application Example 3: A case where the nickel portion of $LiNiO_2$ is substituted with an Ni : Co : Al : Mn (molar ratio) = 80 : 5 : 5 : 10 composition

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A mixed aqueous solution, bearing a total (Ni + Co + Al + Mn) molar number of 4.0 M, was prepared by using nickel nitrate, cobalt nitrate, aluminum nitrate, and manganese nitrate in such a way to realize an Ni : Co : Al : Mn (molar ratio) = 80 : 5 : 5 : 10 composition, and a baked product was subsequently obtained

according to procedures otherwise similar to those in Application Example 1.

[0048]

Incidentally, a partially dried reaction product, obtained midway, bore a composition of $Ni_{0.8}Co_{0.05}Al_{0.05}Mn_{0.1}(OH)_{1.82}(NO_3)_{0.23}\cdot 0.18H_2O)$. An X-ray diffraction analysis of the baked product yielded a pattern analogous to its counterpart registered in 09-0063 of the JCPDS, whereas no peaks other than the peak attributed to $LiNiO_2$ were acknowledged, based on which the pervasion of a crystalline structure, similar to its counterpart of $LiNiO_2$, provided by homogeneously solid-solubilizing, into nickel, components other than nickel, was verified (Figure 2). Moreover, a battery was prepared based on a method similar to its counterpart of Application Example 1, and a recharge-discharge test was conducted under identical conditions. The respective results on the initial recharge-discharge efficiency and initial recharge-discharge curve are shown in Table I and Figure 5.

[0049]

Application Example 4: A case where the nickel portion of $LiNiO_2$ is substituted, without including boron, with a composition otherwise identical to its counterpart of Application Example 3

After a 3.0 M aqueous lithium hydroxide solution had been added to the reaction slurry obtained in Application Example 3 at a quantitative ratio equivalent to an Li/(Ni + Co + Al + Mn) = 1.05 molar ratio, the obtained mixture was spray-dried. The

obtained dried gel was charged into an alumina board [sic: Presumably "boat"?] and then baked, while oxygen was being permeated within the aforementioned tubular furnace, within a temperature range of 750 ~ 850°C over a 15-hour period. An X-ray diffraction analysis of the baked product yielded a pattern analogous to its counterpart registered in 09-0063 of the JCPDS, whereas no peaks other than the peak attributed to $LiNiO_2$ were acknowledged, based on which the pervasion of a crystalline structure similar to its counterpart of $LiNiO_2$ provided by homogeneously solid-solubilizing, into nickel, components other than nickel, was verified (Figure 2). Moreover, a battery was prepared based on a method similar to its counterpart of Application Example 1, and a recharge-discharge test was conducted under identical conditions. The respective results on the initial recharge-discharge efficiency and initial recharge-discharge curve are shown in Table I and Figure 6.

[0050]

Comparative Example 1: A case where the nickel portion of $LiNiO_2$ is substituted with an Ni : Co : Al (molar ratio) = 80 : 15 : 5 composition

    A mixed aqueous solution bearing a total (Ni + Co + Al) molar number of 4.0 M was prepared by using nickel nitrate, cobalt nitrate, and aluminum nitrate in such a way to realize an Ni : Co : Al (molar ratio) = 80 : 15 : 5 composition. Moreover, a 4.0 M sodium hydroxide solution was prepared, and a continuous reaction was induced at a reaction temperature of 25°C over a residing

period of 15 min. by simultaneously charging, in an agitated state, both solutions into a reaction tank at an eventual pH of 9.5 by using a proportioning pump. The obtained reaction product was filtered, and after it had been washed with water (incidentally, a partially dried product bore a composition of $Ni_{0.8}Co_{0.15}Al_{0.05}(OH)_{1.86}(NO_3)_{0.19} \cdot 0.24H_2O$) and then suspended into water, a slurry was obtained by adding, to the obtained suspension, boric acid at a quantitative ratio, with respect to the aforementioned Ni, Co, and Al, equivalent to (Ni + Co + Al) : B molar ratio = 99 : 1. After a 3.0 M aqueous lithium hydroxide solution had been added to this slurry at a quantitative ratio equivalent to an Li/(Ni + Co + Al + B) = 1.05 molar ratio, the obtained mixture was spray-dried. The obtained dried gel was charged into an alumina board [sic: Presumably "boat"?] and then baked, while oxygen was being permeated within the aforementioned tubular furnace, within a temperature range of 750 ~ 850°C over a 15-hour period. An X-ray diffraction analysis of the baked product yielded a pattern analogous to its counterpart registered in 09-0063 of the JCPDS, whereas no peaks other than the peak attributed to $LiNiO_2$ were acknowledged, based on which the pervasion of a crystalline structure similar to its counterpart of $LiNiO_2$ provided by homogeneously solid-solubilizing, into nickel, components other than nickel was verified (Figure 2). Moreover, a battery was prepared based on a method similar to its counterpart of Application Example 1, and a recharge-discharge test was conducted under identical conditions. The respective results on the initial

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recharge-discharge efficiency and initial recharge-discharge curve
are shown in Table I and Figures 5 and 6.

[0051]

<div align="center">Table I</div>

Compound	Composition	Initial recharge-discharge efficiency (%)
Application Example 1	$Li(Ni_{0.8}Co_{0.1}Al_{0.05}Mn_{005})_{0.99}B_{0.01}O_2$	89.9
Application Example 2	$LiNi_{0.8}Co_{0.1}Al_{0.05}Mn_{0.05}O_2$	88.3
Application Example 3	$Li(Ni_{0.8}Co_{0.05}Al_{0.05}Mn_{0.1})_{0.99}B_{0.01}O_2$	87.6
Application Example 4	$LiNi_{0.8}Co_{0.05}Al_{0.05}Mn_{0.1}O_2$	85.6
Comparative Example 1	$Li(Ni_{0.8}Co_{0.15}Al_{0.05})_{0.99}B_{0.01}O_2$	85.1

[0052]

Application Example 5: A case where the nickel portion of $LiNiO_2$ is substituted with an Ni : Co : Al : Mn (molar ratio) = 80 : 12.5 : 2.5 : 5 composition

A mixed aqueous solution bearing a total (Ni + Co + Al + Mn) molar number of 4.0 M was prepared by using nickel nitrate, cobalt nitrate, aluminum nitrate, and manganese nitrate in such a way to realize an Ni : Co : Al : Mn (molar ratio) = 80 : 12.5 : 2.5 : 5 composition, and a baked product was subsequently obtained according to procedures otherwise similar to those in Application Example 1. Incidentally, a partially dried reaction product obtained midway bore a composition of $Ni_{0.8}Co_{0.125}Al_{0.025}Mn_{0.05}(OH)_{1.79}(NO_3)_{0.235}\cdot0.21H_2O$. An X-ray diffraction analysis of the baked product yielded a pattern analogous to its counterpart registered in 09-0063 of the JCPDS, whereas no peaks other than the peak attributed to $LiNiO_2$ were acknowledged, based on which the pervasion of a crystalline structure similar to its counterpart of $LiNiO_2$ provided by homogeneously solid-solubilizing, into nickel, components other than nickel, was verified (Figure 3).

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Moreover, a battery was prepared based on a method similar to its counterpart of Application Example 1, and a recharge-discharge test was conducted under identical conditions. The respective results on the initial recharge-discharge efficiency and initial recharge-discharge curve are shown in Table II and Figure 7.

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[0053]

Comparative Example 2: A case where the nickel portion of $LiNiO_2$ is substituted with an Ni : Co : Al (molar ratio) = 80 : 17.5 : 2.5 composition

A mixed aqueous solution bearing a total (Ni + Co + Al) molar number of 4.0 M was prepared by using nickel nitrate, cobalt nitrate, and aluminum nitrate in such a way to realize an Ni : Co : Al (molar ratio) = 80 : 17.5 : 2.5 composition. Moreover, a 4.0 M sodium hydroxide solution was prepared, and a continuous reaction was induced at a reaction temperature of 25°C over a residing period of 15 min. by simultaneously charging, in an agitated state, both solutions into a reaction tank at an eventual pH of 9.5 by using a proportioning pump. The obtained reaction product was filtered, and after it had been washed with water (incidentally, a partially dried product bore a composition of $Ni_{0.8}Co_{0.175}Al_{0.025}(OH)_{1.84}(NO_3)_{0.185} \cdot 0.23H_2O$) and then suspended into water, a slurry was obtained by adding, to the obtained suspension, boric acid at a quantitative ratio, with respect to the aforementioned Ni, Co, and Al, equivalent to (Ni + Co + Al) : B molar ratio = 99 : 1. After a 3.0 M aqueous lithium hydroxide solution had been added to this slurry at a quantitative ratio equivalent to an Li/(Ni + Co ++ [sic: Presumably "+"] Al + B) = 1.05 molar ratio, the obtained mixture was spray-dried. The obtained dried gel was charged into an alumina board [sic: Presumably "boat"?] and then baked, while oxygen was being permeated within the aforementioned tubular furnace, within a temperature range of 750 ~ 850°C over a 15-hour period. An X-ray

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diffraction analysis of the baked product yielded a pattern analogous to its counterpart registered in 09-0063 of the JCPDS, whereas no peaks other than the peak attributed to $LiNiO_2$ were acknowledged, based on which the pervasion of a crystalline structure similar to its counterpart of $LiNiO_2$ provided by homogeneously solid-solubilizing, into nickel, components other than nickel was verified (Figure 3). Moreover, a battery was prepared based on a method similar to its counterpart of Application Example 1, and a recharge-discharge test was conducted under identical conditions. The respective results on the initial recharge-discharge efficiency and initial recharge-discharge curve are shown in Table II and Figure 7.

[0054]

<div align="center">Table II</div>

Compound	Composition	Initial recharge-discharge efficiency (%)
Application Example 5	$Li(Ni_{0.8}Co_{0.125}Al_{0.025}Mn_{0.05})_{0.99}B_{0.01}O_2$	90.6
Comparative Example 2	$Li(Ni_{0.8}Co_{0.175}Al_{0.025})_{0.99}B_{0.01}O_2$	87.2

[0055]

Application Example 6: A case where the nickel portion of LiNiO$_2$ is substituted with an Ni : Co : Al : Mn (molar ratio) = 70 : 15 : 10 : 5 composition

A mixed aqueous solution bearing a total (Ni + Co + Al + Mn) molar number of 4.0 M was prepared by using nickel nitrate, cobalt nitrate, aluminum nitrate, and manganese nitrate in such a way to realize an Ni : Co : Al : Mn (molar ratio) = 70 : 15 : 10 : 5 composition, and a baked product was subsequently obtained according to procedures otherwise similar to those in Application Example 1. Incidentally, a partially dried reaction product obtained midway bore a composition of $Ni_{0.7}Co_{0.15}Al_{0.1}Mn_{0.05}(OH)_{1.86}(NO_3)_{0.24} \cdot 0.23H_2O$.

[0056]

An X-ray diffraction analysis of the baked product yielded a pattern analogous to its counterpart registered in 09-0063 of the JCPDS, whereas no peaks other than the peak attributed to LiNiO$_2$ were acknowledged, based on which the pervasion of a crystalline structure similar to its counterpart of LiNiO$_2$ provided by homogeneously solid-solubilizing, into nickel, components other than nickel was verified (Figure 4). Moreover, a battery was prepared based on a method similar to its counterpart of Application Example 1, and a recharge-discharge test was conducted under identical conditions. The respective results on the initial recharge-discharge efficiency and initial recharge-discharge curve are shown in Table III and Figure 8.

[0057]

<u>Comparative Example 3: A case where the nickel portion of LiNiO$_2$</u>
<u>is substituted with an Ni : Co : Al (molar ratio) = 70 : 20: 10</u>
<u>composition</u>

A mixed aqueous solution bearing a total (Ni + Co + Al) molar number of 4.0 M was prepared by using nickel nitrate, cobalt nitrate, and aluminum nitrate in such a way to realize an Ni : Co : Al (molar ratio) = 70 : 20: 10 composition. Moreover, a 4.0 M sodium hydroxide solution was prepared, and a continuous reaction was induced at a reaction temperature of 25°C over a residing period of 15 min. by simultaneously charging, in an agitated state, both solutions into a reaction tank at an eventual pH of 9.5 by using a proportioning pump. The obtained reaction product was filtered, and after it had been washed with water (incidentally, a partially dried product bore a composition of $Ni_{0.7}Co_{0.2}Al_{0.1}(OH)_{1.79}(NO_3)_{0.31} \cdot 0.24H_2O$) and then suspended into water, a slurry was obtained by adding, to the obtained suspension, boric acid at a quantitative ratio, with respect to the aforementioned Ni, Co, and Al, equivalent to (Ni + Co + Al) : B molar ratio = 99 : 1. After a 3.0 M aqueous lithium hydroxide solution had been added to this slurry at a quantitative ratio equivalent to an Li/(Ni + Co + Al + B) = 1.05 molar ratio, the obtained mixture was spray-dried. The obtained dried gel was charged into an alumina board [sic: Presumably "boat"?] and then baked, while oxygen was being permeated within the aforementioned tubular furnace, within a temperature range of 750 ~ 850°C over a 15-hour period. An X-ray diffraction analysis of the baked product yielded a pattern

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analogous to its counterpart registered in 09-0063 of the JCPDS, whereas no peaks other than a peak attributed to $LiNiO_2$ were acknowledged, based on which the pervasion of a crystalline structure similar to its counterpart of $LiNiO_2$ provided by homogeneously solid-solubilizing, into nickel, components other than nickel was verified (Figure 4). Moreover, a battery was prepared based on a method similar to its counterpart of Application Example 1, and a recharge-discharge test was conducted under identical conditions. The respective results on the initial recharge-discharge efficiency and initial recharge-discharge curve are shown in Table III and Figure 8.

Table III

Compound	Composition	Initial recharge-discharge efficiency (%)
Application Example 6	$Li(Ni_{0.7}Co_{0.15}Al_{0.1}Mn_{005})_{0.99}B_{0.01}O_2$	91.0
Comparative Example 3	$Li(Ni_{0.7}Co_{0.2}Al_{0.1})_{0.99}B_{0.01}O_2$	85.2

[0058]

   To summarize the foregoing results, it can be gleaned from the results of Table I that the respective recharge-discharge efficiencies of Application Examples 1, 2, 3, and 4 are improved in comparison with Comparative Example 1, whereas comparisons of Application Examples 1 and 3 and Application Examples 2 and 3 reveal that the recharge-discharge efficiency diminishes as the manganese substituting ratio increases and as the cobalt substituting ratio accordingly decreases. Moreover, it can be gleaned from the results of Table II that the recharge-discharge efficiency of Application Example 5 is improved in comparison with Comparative Example 2, whereas it can be likewise gleaned from the results of Table III that the recharge-discharge efficiency of Application Example 6 is improved in comparison with Comparative Example 3, and thus, effects of improving the recharge-discharge efficiency can obviously be acknowledged by partially substituting the cobalt substituting share with manganese.

[0059]

   Moreover, it can be gleaned from the results of Figures 5, 6, 7, and 8 that the discharge potentials of the respective application examples are upped and improved in comparison with the discharge potentials of the respective comparative examples.

[0060]

   The cycle characteristics of the respective samples of Application Examples 1 and 3 and Comparative Example 1 as representative samples are shown in Figure 9 in terms of capacitance retention ratios with respect to the cycle number

(discharge capacitance of each cycle × 100/initial discharge capacitance).

[0061]

Battery preparation and measurement conditions were comparable to those mentioned in Application Example 1. It can be gleaned from the results of Figure 9 that the cycle characteristics exhibited in Comparative Example 1 are either preserved or improved in Application Examples 1 and 3, where the cobalt substituting share of Comparative Example 1 is partially substituted with manganese. Moreover, a group of Application Examples 1 and 3 and Comparative Example 1 and a group of Application Example 5 and Comparative Example 2 were subjected, as representative samples, to high-temperature stability tests in the form of differential thermal measurements shown below. After the battery shown in Application Example 1 had been prepared, said battery was disassembled upon the completion of the initial recharge cycle thereof, and an anode was then retrieved from the same. After three sheets had been punched out of said anode by using a mold with a diameter of 4 mm, the punched anode was washed with dimethyl carbonate and then dried in a vacuum for 2 hours.

[0062]

The anode thus dried was analyzed by using a differential thermal analyzer in an air permeated state at a temperature elevation rate of 10℃/min. for measuring the oxygen dissociation temperature and heat generation peak temperature, whereas the obtained results are shown in Table IV.

[0063]

Table IV

Compound	Initial oxygen dissociation temperature	Heat generation peak temperature
Application Example 1	236.8	233.6
Application Example 3	234.2	235.3
Comparative Example 1	234.0	237.2

[0064]

It can be gleaned from the results of Table IV that no differences in the initial oxygen dissociation temperature and heat generation peak temperature are acknowledged as a result of the comparison of Application Examples 1 and 3 with Comparative Example 1.

[0065]

Table V

Compound	Initial oxygen dissociation temperature	Heat generation peak temperature
Application Example 5	232.8	231.8
Comparative Example 2	231.1	230.0

It can be gleaned likewise from the results of the aforementioned Table V that no differences in the initial oxygen dissociation temperature and heat generation peak temperature are acknowledged as a result of the comparison of Application Example 5 and Comparative Example 2. In other words, it can be gleaned from the results of Table IV that no differences in the initial oxygen dissociation temperature and heat generation peak temperature are acknowledged as a result of the comparison of Application Examples 1 and 3 with Comparative Example 1 and likewise from the results of Table V that no differences in the initial oxygen dissociation temperature and heat generation peak temperature are acknowledged as a result of the comparison of Application Example 5 and Comparative Example 2, and thus, the high-temperature stability can be maintained even if the cobalt

substituting share of each comparative example is partially substituted with manganese.

[0066]
(Effects of the invention)

The present invention provides, by adding, together with cobalt, aluminum, and boron, a specified quantitative ratio of manganese to a lithium-nickel composite oxide used as an anodic active material, an anodic active material for a lithium ion secondary battery with an improved recharge-discharge efficiency and a potential at the time of a discharge without compromising the cycle characteristics and high-temperature stability as well as a non-aqueous electrolytic solution lithium ion secondary battery using said anodic active material.

Brief explanation of the figures

Figure 1: A lengthwise cross-sectional view diagram pertaining to the lithium ion secondary battery of an application example of the present invention.

Figure 2: An XRD pertaining to the respective compounds of Application Examples 1, 2, 3, and 4 and Comparative Example 1.

Figure 3: An XRD pertaining to the respective compounds of Application Example 5 and Comparative Example 2.

Figure 4: An XRD pertaining to the respective compounds of Application Example 6 and Comparative Example 3.

Figure 5: Discharge curves obtained respectively in Application Examples 1 and 3 and Comparative Example 1.

Figure 6: Discharge curves obtained respectively in Application Examples 2 and 4 and Comparative Example 1.

Figure 7: Discharge curves obtained respectively in Application Example 5 and Comparative Example 2.

Figure 8: Discharge curves obtained respectively in Application Example 6 and Comparative Example 3.

Figure 9: Cycle characteristics obtained respectively in Application Examples 1 and 3 and Comparative Example 1.

Figure 1

1.ケース
2.負極
3..グラスフィルター濾紙
4.セパレ・タ
5.ガスケット
6.グラスフィルタ・・濾紙
7.正極
8.ケ・・ス
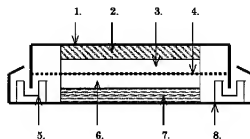
[(1): Case; (2): Cathode; (3): Glass filter paper; (4): Separator; (5): Gasket; (6): Glass filter paper; (7): Anode; (8): Case]

Figure 2
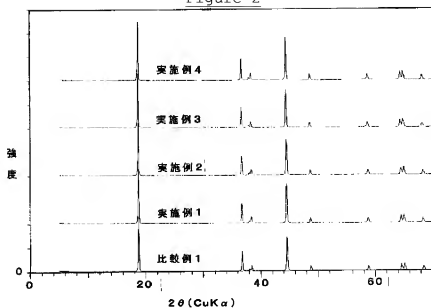
[(A): Intensity; (B): Application Example; (C): Comparative Example]
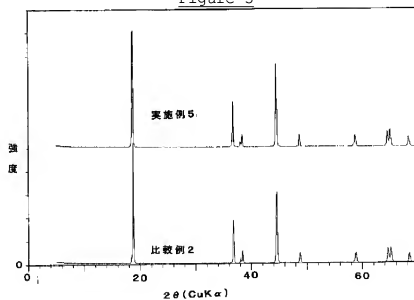
Figure 3

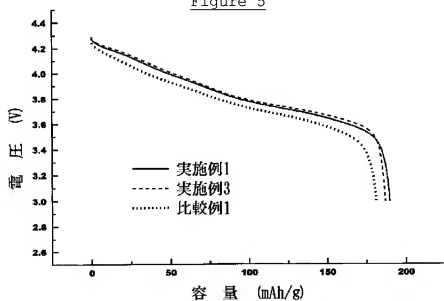[(A): Intensity; (B): Application Example; (C): Comparative Example]

Figure 4
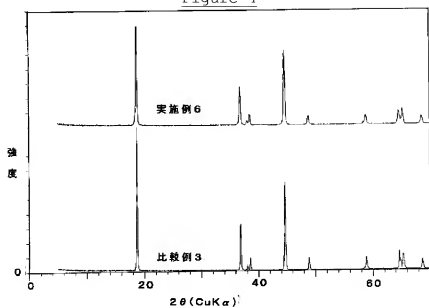
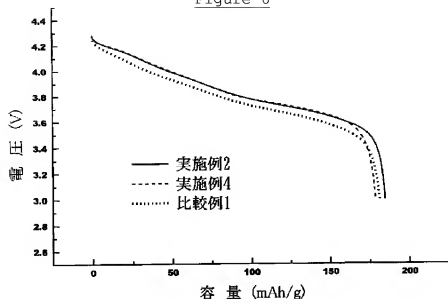[(A): Intensity; (B): Application Example; (C): Comparative Example]

Figure 5

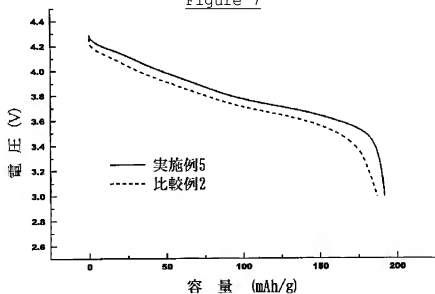[(A): Voltage; (B): Capacitance; (C): Application Example; (D): Comparative Example]

Figure 6

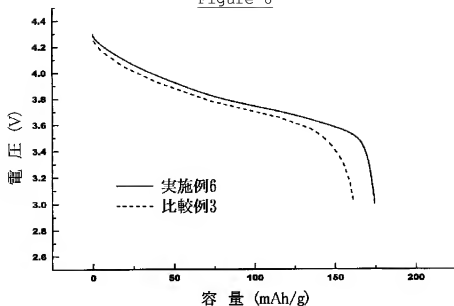[(A): Voltage; (B): Capacitance; (C): Application Example; (D): Comparative Example]

Figure 7

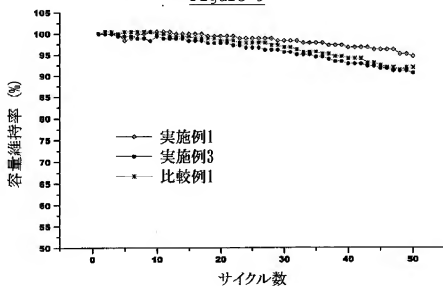[(A): Voltage; (B): Capacitance; (C): Application Example; (D): Comparative Example]

Figure 8

[(A): Voltage; (B): Capacitance; (C): Application Example; (D): Comparative Example]

Figure 9

[(A): Capacitance maintenance ratio; (B): Cycle number; (C): Application Example; (D): Comparative Example]